# A Preliminary Mercury Budget for Narragansett Bay (Rhode Island, USA).

Grace M. Vandal and William F. Fitzgerald

The University of Connecticut Dept. of Marine Sciences Groton, CT USA

## Abstract

The distribution of total Hg (Hg<sub>T</sub>) and reactive (Hg<sub>R</sub>) in Narragansett Bay, fresh water tributaries and point source discharges was determined during a synoptic survey, carried out in April, 1986. A Hg budget which includes fluvial inputs and atmospheric Hg deposition was constructed and the estuarine behavior of Hg assessed.

# 1. Introduction

There is little information regarding the distribution, reactivity and fate of Hg in estuarine environments. Flocculation and coagulation of trace metal (e.g., Fe, Mn, Cu) and organic colloids dissolved in freshwater can occur under conditions of increasing ionic strength (Sholkovitz, 1978) and may result in removal of dissolved constituents during estuarine mixing. Thus, estuaries can serve as traps for riverborne material by way of sediment deposition. Conversely, remobilization of metals bound to particulate matter can occur with increasing salinity. For example, a maxima in dissolved Hg at low salinity (ca. 5 ppt) has been observed in several estuaries, perhaps due to remobilization from particles under turbid conditions. In the Gironde Estuary total dissolved Hg (determined following oxidation with bromine) covaried with turbidity; solubilization of Hg from particles in the turbidity maximum was hypothesized as the source of an upper estuary dissolved Hg maxima (Cossa and Noel, 1987). A similar distribution for dissolved Hg was observed in the Rhône Estuary (Cossa and Martin, 1991). Furthermore, a general decrease in the partition coefficient between particulate and dissolved Hg with increasing salinity provided additional evidence of Hg remobilization from particles. In contrast, removal of total dissolved Hg was observed in the Saint Lawrence Estuary and attributed to adsorption onto solid phase in the turbidity maximum and/or coagulation and of organic colloids (Cossa et al., 1988). Mercury removal within the estuarine mixing zone was also indicated in a study of the Connecticut River Estuary (Gill, 1980). Mercury covaried with dissolved Fe, Hg coprecipatation with Fe was suggested. Here we report the distribution of Hg in Narragansett Bay and its fresh water tributaries determined during a synoptic survey, carried out in April, 1986. A Hg budget which includes fluvial inputs and atmospheric Hg deposition was constructed and the estuarine behavior of Hg assessed.

## 2. Methods

A map of the sampling sites is given in Figure 1. Narragansett Bay is located on the north-eastern coast of the United States. It is a well flushed estuary with an average residence time for water of 24 days. The highly industrialized city of Providence is at the head of the bay. Twelve stations in Narragansett Bay were sampled to cover a salinity gradient from 7 to 32 ppt.

Water, Air, and Soil Pollution 80: 679–682, 1995. © 1995 Kluwer Academic Publishers. Printed in the Netherlands.



Fig. 1. Narragansett Bay is located on the north-eastern coast of the United States. Sampling locations included six stations within the bay (4,5,7,11,13,17) at two depths (0.3 and 13m) and two in the Providence River (1,2). Four rivers which flow into the estuary (Blackstone[BR], Woonasquatucket [WR], Moshassuck [MR], Pawtuxet [PR]) and four point sources (Blackstone Valley Wastewater Treatment Facility (WTF) [BV], Field's Point WTF [FP], East Providence WTF, Narragansett Electric cooling water [NE]) were also sampled.



Collections were made using trace metal clean techniques and a teflon pumping apparatus. Acid-labile Hg (Hg<sub>R</sub>) was determined in filtered (combusted, 0.4  $\mu$ m GFF filter) and unfiltered samples which were acidified to 0.5% HNO<sub>3</sub>. The analysis (SnCl<sub>2</sub> reduction, preconcentration on Au with detection by CVAAS; Gill and Fitzgerald, 1985) was conducted following a 1 month acid digestion period. Total Hg was measured on unfiltered fresh water and upper estuary collections following bromine monochloride oxidation (Bloom and Crecilius, 1983). Strongly bound Hg was defined as the difference between Hg<sub>T</sub> and Hg<sub>R</sub>. Atmospheric deposition of Hg to Narragansett Bay was estimated from average Hg rainwater and atmospheric particulate concentrations measured at Groton, CT (Gill, 1980).

#### 3. Results

The speciation of Hg in the tributaries is given in Figure 2. River waters Hg levels were elevated relative to the saline waters. Unfiltered Hg<sub>T</sub> concentrations ranged from 36 to 150 pM for these urban impacted waters while Hg<sub>R</sub> values were lower (8 to 29 pM). Strongly bound Hg forms were a major fraction of the fresh water Hg. Point source Hg<sub>T</sub> concentrations ranged from 42 to 346 pM of which >50% was strongly bound. Strongly bound comprised 25% of the total Hg, in



Figure 2. The speciation of Hg in the tributaries and upper bay stations (Stations 1, 4 and 5).

the upper bay collections (Stations 1, 4 and 5) indicating loss of this component in the upper estuary. A mean  $Hg_R$  concentration for the fresh water end-member was estimated based on the measured  $Hg_R$  concentration for each source multiplied by it discharge rate at the time of this study. The flow-weighted mean Hg concentrations are used to assess the behavior of the Hg fractions across the salinity gradient. Within the estuary unfiltered Hg<sub>R</sub> in was highest at the head of the estuary (18.5 pM) and decreased seaward (5.5 pM); removal at low salinity (ca.7ppt) was indicated. The role of suspended matter in Hg transport is supported by the strong correlation of Hg<sub>R</sub> in unfiltered collections with turbidity (r=0.99) and total suspended load (r=0.96). Dissolved Hg<sub>R</sub> ranged from 2 to 17 pM and covaried inversely with salinity suggesting conservative mixing.

#### 4. A Preliminary Budget

A Hg budget for Narragansett Bay was developed from this limited data set and is presented in Figure 3. The Taunton River flux was approximated assuming a Hg<sub>R</sub> concentration of 95 pM, the average of the four rivers sampled. Fluvial inputs contributed 61 g d<sup>-1</sup>, equivalent to 69% of the total Hg flux into Narragansett Bay. The flux from point sources was 18.5 g d<sup>-1</sup> (21%). Atmospheric deposition was estimated at 10 g d<sup>-1</sup> (10%) assuming an average rain concentration of 50 pM (Fogg and Fitzgerald, 1979); 328 km<sup>2</sup> for the are of the bay (Pilson, 1985); and 100 cm of rain per year. Tidal exchange removes approximately 49 g d<sup>-1</sup>. This calculation is based on 406 x 10<sup>6</sup> m<sup>3</sup> as the volume of the tidal prism<sup>2</sup>; the concentration of the inflowing water is taken as 5.5 pM (Station 22); and a fresh water entrainment rate of 1% per tidal cycle results in elevation of the outgoing water to 5.8 pM. A balanced budget requires a flux to the sediment of 40 g d<sup>-1</sup>. In summary, approximately 50% of the Hg entering the bay is exported by tidal exchange and 50% retained within the estuarine sediments.



Figure 3. A preliminary Hg budget for Narragansett Bay.

## 5. Conclusions

A strongly bound form of Hg was evident in river and point source collections. This component was absent from saline waters and appeared to removed at the salt water interface. Dissolved  $Hg_R$  mixed conservatively along the salinity gradient. However, removal of  $Hg_R$  associated with suspended material at low salinities was suggested. A preliminary budget was constructed for Narragansett Bay Rivers contribute the principal Hg flux to the bay followed by point source discharges and atmospheric deposition. Our calculations indicate that 50 % of the Hg entering the estuary is deposited and 50% is exported via tidal flushing.

#### References

Bloom, N.S. and Crecilius, E.A.: 1983, Marine Chem. 14, 49-59.
Cossa, D. and Martin, J.M.: 1991, Marine Chem. 36, 291-302.
Cossa, D., Gobeil, C. and Courau, P.: 1988, Estuarine, Coastal and Shelf Sci. 26, 227-230.
Cossa, D. and Noel, J.: 1987, Marine Chem. 20, 389-396.
Fogg, T. and Fitzgerald, W.F.: 1979, J. Geophysical Res. 84, 6987-6989.
Gill, G. A. and Fitzgerald, W.F.: 1987, Marine Chem. 20, 227-243.
Gill, G.A. : 1980, PhD Thesis, The Univ. of Connecticut.
Pilson, M.E.: 1985. Estuaries 8, 2-14.
Sholkovitz, E.R.: 1978, Geochim. Cosmochim Acta 40, 831-845.

This is contribution no. 261 from the Marine Sciences Institute, The Univ. of Connecticut.

682